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# Synthesis and Structural Chemistry of Au(III)-Substituted $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$

A.F. Hepp, J.R. Gaier, J.J. Pouch, and A. Banerjea  
*Lewis Research Center*  
*Cleveland, Ohio*

and

P.D. Hambourger  
*Cleveland State University*  
*Cleveland, Ohio*

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# SYNTHESIS AND STRUCTURAL CHEMISTRY OF Au(III)-SUBSTITUTED $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$

A. F. Hepp, J. R. Gaier, J. J. Pouch, and A. Banerjea  
NASA Lewis Research Center, M.S. 302-1, Cleveland, OH 44135

P.D. Hambourger  
Physics Department, Cleveland State University, Cleveland, OH 44115

## ABSTRACT

Gold-substituted superconductors,  $\text{Ba}_2\text{Y}(\text{Au}_x\text{Cu}_{1-x})_3\text{O}_{7-\delta}$  ( $x = 0 - 0.1$ ) have been synthesized. For  $x = 0.1$ , there is no change in the  $a$  and  $b$  lattice parameters ( $a = 3.826 \text{ \AA}$  and  $b = 3.889 \text{ \AA}$ ) but a  $0.06 \text{ \AA}$   $c$  axis expansion to  $11.75 \text{ \AA}$  is observed. Substituted gold is found to be trivalent by XPS. Replacing Cu(1) in the copper oxide chain with a slight reordering of oxygen is consistent with  $c$  axis expansion. The formal charge of the site remains trivalent; remaining Cu in the chains may be reduced resulting in an oxygen stoichiometry  $\leq 7$ . A small effect on  $T_c$  ( $89 \text{ K}$  for  $x = 0.10$ ) is observed upon gold substitution.

## INTRODUCTION

Since reports of the synthesis<sup>1</sup> and structure<sup>2</sup> of the superconductor  $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ , many copper substitution studies have appeared. These efforts have mainly focused on ions of the first row transition<sup>3-6</sup> and Group IIIB<sup>5-7</sup> metals. Typically, trivalent ions substitute at the Cu(1) site in copper oxide chains and induce an orthorhombic/tetragonal transition while divalent ions substitute in copper oxide planes and do not cause a major structural shift. Oxygen ordering is disrupted by the structural requirements of substituting ions, lowering  $T_c$ , particularly for Cu(2) substitution (e.g.  $\text{Zn}^{2+}$ ).<sup>3</sup>

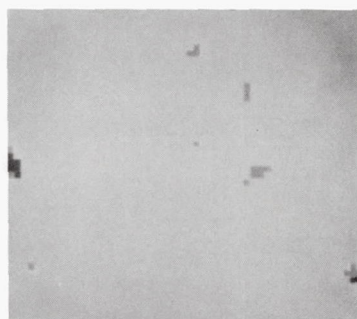
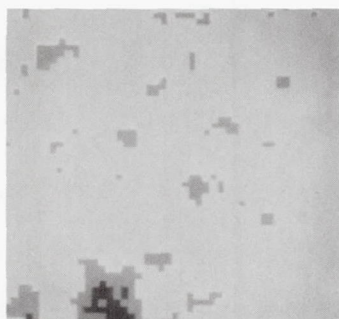
An understanding of the structural and superconducting properties of metal doped perovskite superconductors is critical not only for possible insights into mechanisms of ceramic superconductivity but also because these phases are often formed during synthesis of useful superconducting structures (i.e. thin films<sup>7</sup> or composites<sup>8</sup>). We present results on the formation and properties of Au(III)-substituted  $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ . We discuss these results as they relate to the chemistry of Au(III) and the use of gold-containing superconducting materials.

## EXPERIMENTAL

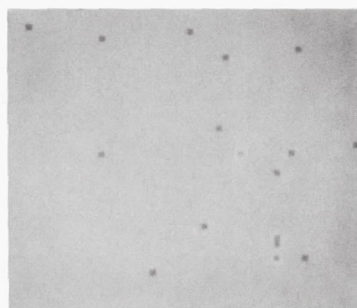
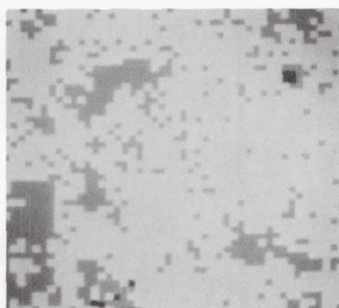
The superconducting oxides were synthesized from  $\text{CuO}$ ,  $\text{BaO}_2$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{Au}_2\text{O}_3$  powders ground together and fired at  $950^\circ\text{C}$  for 32 hours.  $\text{BaO}_2$  was used to prevent gold reduction; it was also used to optimize doping homogeneity. This is shown in figure 1 for an undoped superconductor and discussed elsewhere.<sup>9</sup> XPS measurements were made on a Perkin-Elmer XPS-AES-SIMS instrument. A. C. susceptibility and d. c. resistance were used to measure  $T_c$ . X-ray powder data were collected on a diffractometer using monochromated  $\text{Cu K}_\alpha$  radiation.

SYNTHESIZED WITH  $\text{BaCO}_3$

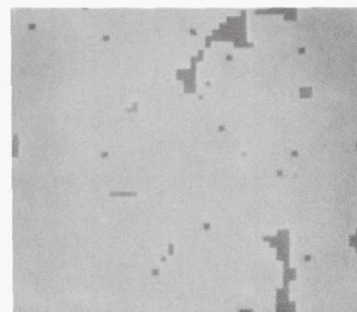
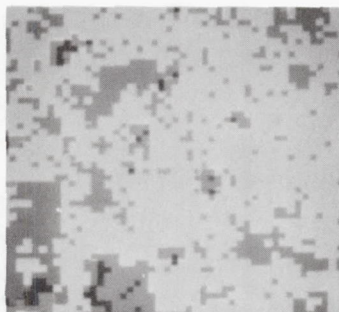
SYNTHESIZED WITH  $\text{BaO}_2$



(A) VARIATION IN Ba PER UNIT Cu.



(B) VARIATION IN Cu PER UNIT Y.



0.0 12.5 25.0 37.5 50.0 62.5 75.0 0.0 12.5 25.0 37.5 50.0 62.5 75.0  
MICROMETERS

(C) VARIATION IN Ba PER UNIT Y.

FIG. 1. Difference Energy Dispersive X-Ray Spectropic (EDXS) images show the variations of composition across the sample for Cu, Ba, and Y as noted above. Dark areas indicate an excess of one of the elements with respect to the other, samples prepared with  $\text{BaO}_2$  are more homogeneous than those prepared with  $\text{BaCO}_3$ .



## RESULTS

Structural data for a series of  $\text{Ba}_2\text{Y}(\text{Au}_x\text{Cu}_{1-x})_3\text{O}_{7-\delta}$  superconductors is shown in figure 2. The assignment of the trivalent oxidation state is made by virtue of XPS data which shows a shoulder at 87 eV. This 3 eV shift from metallic gold is characteristic of the trivalent state.<sup>10</sup> Maintenance of the integrity of the a-b plane and expansion of the c axis is the most striking result of our study. These results stand in stark contrast to earlier results with trivalent metal ion substitution which produces a tetragonal structure for Fe,<sup>4,6</sup> Co,<sup>4,6</sup> Al,<sup>6,7</sup> and Ga<sup>5</sup> for  $x < 0.10$ . An interesting illustration of the lengthening of the c axis is shown in figure 3. As the mole percent of Au(III) is increased from  $x = 0$  to 0.05 and then to 0.10, the 006 peak in the x-ray pattern shifts to lower  $2\theta$  values while the 020 and 200 peaks remain stationary. This destroys the coincidence between the 006 and 020 peaks in the x-ray pattern of the native structure.

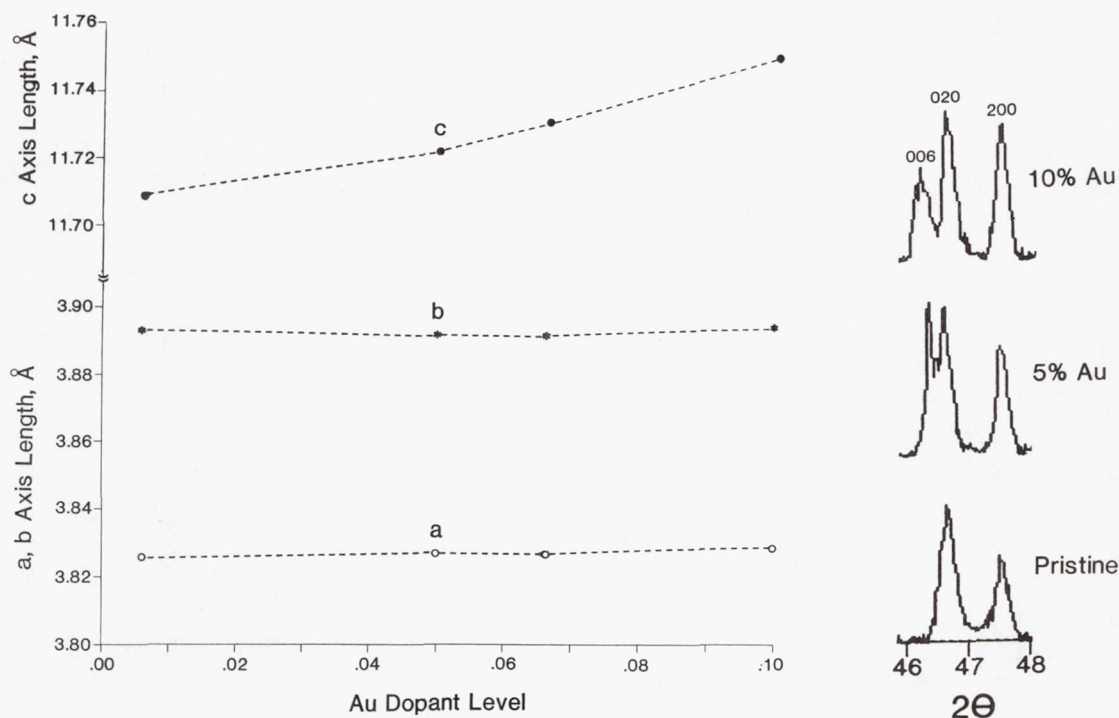


FIG 2. Lattice constants of Au (III)-substituted  $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$  vs. Au (III) substitution level. Note that while a and b axes remain constant, c axis expands 0.06 Å. See text for discussion.

FIG. 3. XRD data for Au (III)-substituted  $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ .

A brief summary of structural and electrical data for well characterized metal-substituted  $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$  is outlined in Table I and includes data from this study. As noted above, trivalent metal ions predominantly substitute for copper at the Cu(1) site along chains although Fe and Co may also dope at the Cu(2) site.<sup>6</sup> Neutron diffraction, powder XRD, and thermogravimetric analysis (TGA) data on the effect of metal doping on Cu(1) bound oxygen removal point to doping in the a-b plane for divalent metal ions.<sup>5,6</sup>

TABLE I.

Structural and Electronic Data\* of Metal-Substituted  $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$

Metal Ion	Electronic Structure	Metal Substitution Level**	Substitution Location	Molecular Structure	$T_c(\text{K})^{***}$
$\text{Al}^{3+}$	$2s^2 2p^6$	0.04 0.07	$\text{Cu}(1)^{7a}$ $\text{Cu}(1)^{7a}$	Tetr. <sup>6,7</sup> Tetr. <sup>7</sup>	$51^7$ $<4^7, 85^6$
$\text{Fe}^{3+}$	$3d^5$	0.03 0.07 0.10 0.17	$\text{Cu}(1)^{6b}$ $\text{Cu}(1,2)^{6b}$ $\text{Cu}(1,2)^{6b}$ $\text{Cu}(1)^{4a}$	Tetr. <sup>6</sup> Tetr. <sup>6</sup> Tetr. <sup>6</sup> Tetr. <sup>4,6</sup>	$76^6$ $49^6$ $38^3$ $0^{4,6}$
$\text{Co}^{3+}$	$3d^6$	0.03 0.10 0.27 0.33	$\text{Cu}(1)^{6c}$ $\text{Cu}(1)^{6c}$ $\text{Cu}(1,2)^{6d}$ $\text{Cu}(1)^{7a}$	Tetr. <sup>6</sup> Tetr. <sup>6</sup> Tetr. <sup>6</sup> Tetr. <sup>4,6</sup>	$73^6$ $22^3$ $0^6$ $0^{4,6}$
$\text{Ni}^{2+}$	$3d^8$	0.10	$\text{Cu}(2)^{6c}$	Orth. <sup>6</sup>	$40^6, 66^3$
$\text{Zn}^{2+}$	$3d^{10}$	0.10	$\text{Cu}(2)^{5d}$	Orth. <sup>5,6</sup>	$20^5, 45^6$
$\text{Ga}^{3+}$	$3d^{10}$	0.07	$\text{Cu}(1)^{5d}$	Tetr. <sup>5</sup>	$60^5$
$\text{Au}^{3+}$	$5d^8$	0.01 0.05 0.07 0.10	$\text{Cu}(1)^e$	Orth.	$92^{f,g}$ $89^f$ $92^f, 90^g$ $89^f$

\* - Data obtained from references and/or determined by: <sup>a</sup> - XRD single crystal structure; <sup>b</sup> - Mössbauer; <sup>c</sup> - TGA; <sup>d</sup> - Neutron diffraction of powder; <sup>e</sup> - XRD powder pattern; <sup>f</sup> - A. C. susceptibility; or <sup>g</sup> - D. C. resistance. \*\* - Metal substitution level in mole fraction per copper atom. \*\*\* - Differences may be due to sample inhomogeneity or lack of oxygen annealing, see references 6 and 7.



## DISCUSSION

Structural considerations have been mentioned by several groups as leading to oxygen disordering. For example, substitution of  $\text{Al}^{3+}$ , which prefers octahedral coordination eventually drives the structure tetragonal to achieve a more stable Al coordination environment,<sup>7</sup> the same argument would also apply to  $\text{Ga}^{3+}$ .<sup>5</sup>  $\text{Fe}^{3+}$  and  $\text{Co}^{3+}$  prefer tetrahedral or octahedral and octahedral coordination, respectively and have been noted to cause similar disordering.<sup>4</sup> The differing effects of  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  may be in the increased tolerance of  $d^8$  ions for square pyramidal coordination as opposed to  $d^{10}$   $\text{Zn}^{2+}$  which tends towards tetrahedral coordination to minimize ligand repulsion.

With these considerations in mind, the influence of  $\text{Au(III)}$  is consistent with the observed substitution chemistry of perovskite superconductors and the chemistry of trivalent gold.  $\text{Au(III)}$  is known to form square planar complexes almost exclusively due to the large difference in energy between the unfilled  $d_{x^2-y^2}$  and the filled  $d_{z^2}$  orbitals of the  $5d^8$  ion. The expansion of the c axis can be attributed to the larger size of the  $\text{Au(III)}$  in the same way that a slight decrease in the c axis was noted for Al substitution.<sup>7</sup> However, we did not observe an increase of the b axis which would be expected for simple substitution at the  $\text{Cu(1)}$  site.

We believe there is a slight reordering of oxygen involving the a-b plane accompanied by reduction of the other Cu ions to  $\text{Cu(I)}$ . More detailed studies are in progress to elucidate the exact nature of the oxygen ordering at the  $\text{Au(III)}$  site. We also considered  $\text{Au(III)}$  doping at the rare earth site or simply not substituting into the lattice. However, neither result is consistent with a slight decrease in oxygen stoichiometry (*vide infra*) or the lack of a second phase such as  $\text{Y}_2\text{BaCuO}_5$ <sup>11</sup> expected due to our reaction stoichiometries.

Reduction of  $\text{Cu(1)}$  on the chain to  $\text{Cu(I)}$  has also been observed to increase the c lattice parameter.<sup>6</sup> In fact it has been noted that trivalent doping may be accompanied by either oxygen increase or reduction of Cu on the chain to  $\text{Cu(I)}$ .<sup>4,6</sup> Our crude weight loss results from reaction data indicate a slight decrease in oxygen stoichiometry. These results can be contrasted to other trivalent metal ion substitutions which exhibit oxygen stoichiometries  $\geq 7$  for Co,<sup>4,6</sup> Fe,<sup>4,6</sup> Ga,<sup>5</sup> or Al.<sup>6,7</sup> It is interesting to note that Zn doping may actually lead to a slight decrease in oxygen which correlates to Zn concentration ( $\delta = 0.3$  when  $x = 0.3$ ) and to the preferred tetrahedral coordination of  $\text{Zn}^{2+}$ .<sup>6</sup> Substitution of  $\text{Au(III)}$  leads to formation of two coordinate  $\text{Cu(I)}$  which may result in a slight loss of oxygen along the chains.

Data from other substitution studies indicate that doping in the a-b plane has a greater impact on superconductivity than doping on the chains.<sup>3-7</sup> The impact of trivalent metal ion doping arises when the electronic configuration of the substituting ions induces a structural change, an oxygen disordering and influences the structure of  $\text{Cu(II)}$

ions in the a-b plane. Au(III) substitution does not perturb the Cu(2) planes because its square planar geometry (consistent with its electronic configuration) does not induce an oxygen reordering sufficient to cause a structural change.

### CONCLUSIONS

The a and b axes of the unit cell remain constant at 3.826 Å and 3.893 Å, respectively, and the c axis expands from 11.69 Å to 11.75 Å upon substitution of 10 mole percent Au at Cu(1) on copper oxide chains. The c axis expansion correlates well with the doping level but the lack of b axis expansion could be the result of a slight oxygen reordering. The lack of a significant structural change upon substitution at the Cu(1) chains is reflected in the lack of a significant lowering of  $T_c$ . The observed structural chemistry of Au substituted into  $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$  is consistent with known perovskite substitution chemistry and the well known chemistry of Au(III). These results support earlier evidence of the importance of copper oxide planes for superconductivity in the perovskite superconductors<sup>5,6</sup> and point to Cu(1) chains as having more of a structural as opposed to an electronic influence on the mechanism superconductivity in perovskite superconductors. Finally, our results indicate that Au(III) substitution chemistry makes gold an excellent candidate for multi-phased structures containing perovskite superconductors.<sup>8,12</sup>

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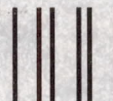
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